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(21) International Application Number: PCT/JP96/02987 (22) International Filing Date: 16 October 1996 (16.10.96) (30) Priority Data: 7/266866 16 October 1995 (16.10.95) JP (71) Applicant (for all designated States except US): W.R. GRACE & CO. - CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): NISHIKAWA, Katsue [JP/JP]; 2-11-28, Nishitsuruma, Yamato-shi, Kanagawa-ken 242 (JP). HAGIWARA, Youshichi [JP/JP]; 5-203, 4-1, Miyanosato, Atsugi-shi, Kanagawa-ken 243-02 (JP). (74) Agent: HOSOKAWA, Shinya; Yuasa and Hara, Section 206, New Ohtemachi Building, 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100 (JP).		(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, HU, IL, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: METHOD FOR PRODUCING WATER-DISPERSIBLE RESIN, AND AQUEOUS COATING COMPOSITION CONTAINING IT			
(57) Abstract			
<p>The object of the present invention is to provide a stable water-dispersible resin, using a reduced amount of an organic solvent or not using any organic solvent, and to provide an aqueous coating composition comprising the water-dispersible resin and capable of forming on metallic substrates a protective film having excellent characteristics. The invention provides a method for preparing a water-dispersible resin comprising: (1) preparing an aqueous dispersion of a modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule, from an epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000, (2) polymerizing, in the aqueous dispersion, at least one unsaturated monomer component that indispensably comprises an unsaturated compound having at least one unsaturated group and at least one carboxyl group in one molecule, and (3) adding to the resulting polymer from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline substance to thereby neutralize the carboxyl groups of the polymer.</p>			

## DESCRIPTION

METHOD FOR PRODUCING WATER-DISPERSIBLE RESIN,  
5 AND AQUEOUS COATING COMPOSITION CONTAINING IT

TECHNICAL FIELD

The present invention relates to a coating composition for  
metallic substrates. More precisely, it relates to an aqueous  
10 coating composition which is useful as a coating composition for  
forming a protective film on the inside and outside of metallic  
cans, or as a coating composition for precoated metal sheets that  
are generally referred to as precoat metals.

BACKGROUND ART

15 Various coating compositions are applied to the inside and  
the outside of metallic cans for canned (or tinned) goods and  
also to metallic substrates themselves to be formed into metallic  
cans, in order to prevent the metals from being corroded by the  
contents, to prevent the metals from dissolving into the contents  
20 and to prevent the outside prints from being damaged. In  
addition, various coating compositions are also used for  
repairing the damaged coats as formed during the production of  
coated cans. For these purposes, heretofore, coating  
compositions comprising epoxy resins and curing agents for the  
25 resins and vinyl-type coating compositions have been popularly  
used, as having excellent adhesion to metallic substrates,  
excellent corrosion resistance and excellent flavor  
characteristics. These epoxy-type coating compositions and

vinyl-type coating compositions are prepared by dissolving the constitutive components in organic solvents.

In producing coated metallic cases, precoated metal sheets may be worked in order to obviate the need for coating the shaped cases later. Precoated metal sheets to be used for this purpose are referred to as precoat metals.

Recently, in view of environmental problems, pollution caused by the vaporization of organic solvents and about the health and safety of workers, the conversion of various organic solvent-type coating compositions into aqueous coating compositions has been promoted. This applies also to coating compositions for metals. For example, there have heretofore been developed compositions to be prepared by grafting an epoxy resin with an acrylic polymer having carboxyl groups, then neutralizing the carboxyl groups in the resin with an alkali, and dispersing the resin in water, such as those disclosed in Japanese Patent *Laid-Open No. 62-178691* and Japanese Patent Publication No. 59-37287; coating compositions to be prepared by neutralizing a reaction product of an epoxy resin and a polymer having carboxyl groups with an alkali, followed by dispersing it in water, such as those disclosed in Japanese Patent Publication Nos. 63-41934 and 59-37026; and compositions to be prepared by dispersing an epoxy resin and a curing agent for the resin in water along with an emulsifier of an acrylic polymer having carboxyl groups, such as those disclosed in Japanese Patent Application Laid-Open No. 63-275675.

However, the aqueous coating compositions as obtained according to the methods mentioned above are problematic in that

they are poorly stable and that the production of these requires high temperatures, long-time reaction steps and hardly-controllable reaction conditions. In addition, after the preparation of the compositions, the organic solvent existing  
5 therein is removed in order to reduce the organic solvent content of the compositions. This results in still other problems in that the production costs increase and that the organic solvent vaporizes during the process of removing it.

DISCLOSURE OF INVENTION

10 The present invention has been made in order to solve the above-mentioned problems, and its object is to provide a water-dispersible resin which can be produced with a significantly reduced amount of an organic solvent and from which, even when formulated into a coating composition, the removal of the organic  
15 solvent is unnecessary, and also to provide an aqueous coating composition comprising the resin, which has good storage stability and exhibits good flavor characteristics, adhesiveness, boiling water resistance and workability when used as a coating composition for metals.

20 Specifically, the present invention relates to a method for preparing a water-dispersible resin, which comprises (1) preparing an aqueous dispersion of a modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule, from an epoxy resin having at least two 1,2-epoxy  
25 groups in one molecule and having an epoxy equivalent of from 100 to 5,000, (2) polymerizing, in the aqueous dispersion, at least one unsaturated monomer component that indispensably comprises an unsaturated compound having at least one unsaturated group and

at least one carboxyl group in one molecule, and (3) adding to the resulting polymer from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline substance to thereby neutralize the carboxyl groups of the polymer. The invention also relates to an aqueous coating composition comprising the water-dispersible resin.

In the method of the present invention, any and every known epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000 can be employed. Examples of the epoxy resin include glycidyl ether-type epoxy resins such as typically bisphenol A-type epoxy resins, and glycidyl polycarboxylates, glycidylamine-type epoxy resins, linear aliphatic epoxy resins, alicyclic epoxy resins, and novolak-type epoxy resins. These epoxy resins can be used singly or as mixtures of two or more.

In the method of the present invention, commercially-available epoxy resins such as those mentioned above can be directly used, but can also be used after having been modified under heat with epoxy resin modifiers. One example of the modification is to modify an epoxy resin having two terminal 1,2-epoxy groups in one molecule to thereby increase its molecular weight to that of a higher polymer. As examples of epoxy resin modifiers to be used for this purpose of increasing the molecular weight of an epoxy resin into a higher polymer, mentioned are bisphenols such as bisphenol A, bisphenol F; vegetable oil fatty acids such as soybean oil fatty acids, dehydrated castor oil, tall oil fatty acids; dimer acids; and mixtures of these. If

desired, aromatic carboxylic acids, such as benzoic acid and p-tert-benzoic acid, can also be used together with the modifiers. In addition, a part of the epoxy groups in the epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000 can be reacted with a higher fatty acid, such as stearic acid, palmitic acid or stearic acid, to thereby improve the flexibility of the resin.

In the first step of the method of the present invention that is to prepare an aqueous dispersion of a modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule, from an epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000, for example, the epoxy resin is first reacted with a tertiary amine to thereby convert the epoxy groups into quaternary ammonium hydroxide groups, and then reacted with an organic acid to thereby convert the quaternary ammonium hydroxide groups into quaternary ammonium carboxylate groups, and the resulting modified epoxy resin is dispersed in water.

Accordingly, the first aspect of the present invention is a method for preparing a water-dispersible resin comprising the steps of:

(a) reacting an epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000 with from 1 to 1.5 equivalents, per equivalent of the epoxy resin, of a tertiary amine, in the presence of water in a solvent, to prepare a modified epoxy resin having at least two quaternary ammonium hydroxide groups in one molecule;

(b) reacting the modified epoxy resin having at least two

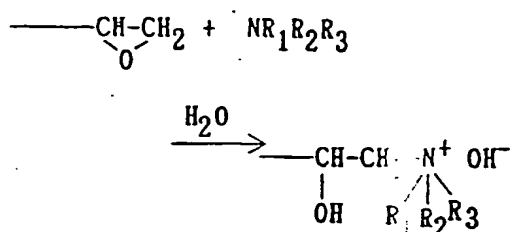
quaternary ammonium hydroxide groups in one molecule as obtained in the previous step (a) with an organic acid having at least one carboxyl group in one molecule to prepare a modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule;

(c) dispersing in water the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule as obtained in the previous (b);

(d) polymerizing, in the aqueous dispersion of the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule as obtained in the previous step (c), at least one unsaturated monomer component that indispensably comprises an unsaturated compound having at least one unsaturated group and at least one carboxyl group in one molecule; and

(e) adding to the resulting polymer from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline compound, to thereby neutralize the carboxyl groups in the polymer.

In the method of the first aspect of the present invention mentioned above, an epoxy resin having at least two 1,2-epoxy groups in one molecule is first reacted with a tertiary amine in the presence of water in a solvent, thereby converting the terminal epoxy groups of the epoxy resin into quaternary ammonium hydroxide groups, to prepare a modified epoxy resin having at least two quaternary ammonium hydroxide groups in one molecule, in the step (a). This reaction can be represented by the following chemical reaction formula:



The reaction of the epoxy resin with the tertiary amine to produce quaternary ammonium hydroxide groups is conducted generally at a temperature falling between 5°C and 100°C, after the epoxy resin has been dissolved in a suitable solvent. If the temperature is lower than 5°C, the reaction could not be promoted



and will take much time. If it is higher than 100°C, some undesirable side reactions will occur and the reaction product may gel.

Any and every known organic solvent capable of dissolving epoxy resins can be used for the reaction of the epoxy resin with the tertiary amine. Desirably, however, used are alcoholic solvents capable of dissolving both the starting epoxy resin and the quaternary ammonium hydroxide produced. Such alcoholic solvents include, for example, cellosolve solvents such as methyl cellosolve, ethyl cellosolve, and butyl cellosolve; diethylene glycol solvents such as carbitol, and butyl carbitol; and monoesters of propylene glycol. The unsaturated monomer component that shall be used as the reactant in the following step of the method of the present invention can also be used as the reaction solvent for the reaction of the epoxy resin with the tertiary amine.

The reaction time necessary for the formation of the quaternary ammonium hydroxide varies, depending on the epoxy resin used, the tertiary amine used, the organic solvent used, the concentration of the reactants in the organic solvent, and the reaction temperature. In general, however, it may be from 5 minutes to 12 hours.

In the method of the present invention, the organic solvent is required only in the step (a) of reacting the epoxy resin with the tertiary amine or in another step of reacting the epoxy resin with the tertiary amine and an organic acid that shall be mentioned hereinunder. Accordingly, by minimizing the amount of the organic solvent to be used in this stage, the organic solvent

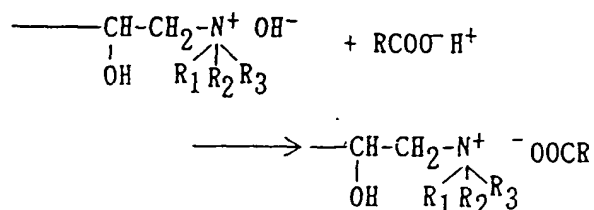
content of the final product can be reduced. A suitable amount of the organic solvent to be used varies, depending on the molecular weight of the epoxy resin used, but may well be such that the solvent can completely dissolve the epoxy resin to give an epoxy resin solution capable of being stirred and reacted at predetermined reaction temperatures. The amount of the solvent may be generally such that the epoxy resin solution can have a resin concentration of from 60 to 90 % by weight. The reaction for converting the terminal epoxy groups of the epoxy resin into quaternary ammonium hydroxide groups is promoted more rapidly, if the reactant concentration is higher or, that is, the concentration of the epoxy resin solution is higher. From this viewpoint, it is desirable to reduce the amount of the organic solvent to be used. As has been mentioned hereinabove, the unsaturated monomer component that shall be used as a reactant in the following step of the method of the present invention can also be used as the solvent to dissolve the epoxy resin. If the monomer is used in this manner, no organic solvent is used in the method of the present invention. Thus, an absolute aqueous resin can be produced.

Water is indispensable in the step (a) of the method of the invention of forming the quaternary ammonium hydroxide groups. The amount of water necessary for the formation of the quaternary ammonium hydroxide groups in the invention may be satisfactorily brought by water in air that shall be taken into the reactor and thus into the reaction system during the reaction, or by water to be contained in the epoxy resin, the tertiary amine and the organic solvent to be used. In general, however, it is desirable

to add water to the reaction system in an amount of 30 times by weight or less of the tertiary amine used in the reaction. Addition of too much water over this range to the reaction system is unfavorable, as it retards the reaction.

5 In the next step (b), an organic acid having at least one carboxyl group in one molecule is added to the modified epoxy resin having at least two quaternary ammonium hydroxide groups in one molecule, thus obtained in the previous step (a), to thereby attain the ion exchange between the quaternary ammonium  
10 hydroxide group and the carboxyl group to give a different modified epoxy resin having quaternary ammonium carboxylate groups.

The ion exchange reaction between the quaternary ammonium hydroxide group and the carboxyl group can be represented by the  
15 following chemical reaction formula:



The organic acid having at least one carboxyl group in one molecule, which is used in the step (b) of the method of the present invention, includes, for example, aliphatic monocarboxylic acids such as formic acid, acetic acid, propionic  
20 acid, butyric acid, valeric acid, caproic acid, oleic acid, and lactic acid; aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, and sebacic acid; aromatic carboxylic acids such as benzoic

acid, toluic acid, and naphthoic acid; and mixtures of two or more of these. However, such are not limitative.

As examples of the organic acid having at least one carboxyl group in one molecule that are especially preferably used in the method of the present invention, mentioned are unsaturated carboxylic acids capable of being further polymerized after having acted on the quaternary ammonium hydroxide groups to convert them into the quaternary ammonium carboxylate groups. Such unsaturated carboxylic acids include, for example, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, itaconic acid, fumaric acid, maleic acid, citraconic acid, and succinic acid.

The amount of the organic acid to be used shall be from 0.3 to 6.0 moles, per mole of the quaternary ammonium hydroxide groups as converted from the terminal hydroxyl groups of the epoxy resin. If the amount of the organic acid used is less than this range, it is difficult to disperse the quaternary ammonium carboxylates formed in water. If, however, it is over the range, the characteristics, especially the water-resistance of the film to be finally formed from the aqueous coating composition comprising the resin will be lowered.

In the method of the present invention, the reaction of the modified epoxy resin having quaternary ammonium hydroxide groups as derived from the epoxy resin with the organic acid having at least one carboxyl groups in one molecule to produce the different modified epoxy resin having quaternary ammonium carboxylate groups can be attained merely by mixing the two at room temperature. However, in order to further ensure the mixing

and the reaction of the two, it is more desirable to heat and stir the reaction system at from room temperature to 100°C for from 5 minutes to 2 hours.

5 Apart from the above-mentioned process of the invention for converting the epoxy groups of the epoxy resin into the quaternary ammonium carboxylate groups via the quaternary ammonium hydroxide groups, it is also possible to employ a one-step process of reacting an epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of  
10 from 100 to 5,000 with both a tertiary amine and an organic acid such as those mentioned hereinabove to produce the quaternary ammonium carboxylate groups.

Accordingly, the second aspect of the present invention is a method for producing a water-dispersible resin comprising the  
15 steps of:

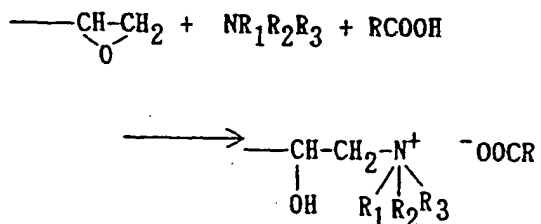
(i) reacting an epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000 with from 1 to 1.5 equivalents, per equivalent of the epoxy resin, of a tertiary amine and an organic acid, in the  
20 presence of water in a solvent, to prepare a modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule;

(ii) dispersing in water the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule  
25 as obtained in the previous step (i);

(iii) polymerizing, in the aqueous dispersion of the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule as obtained in the previous

5 (iv) adding to the resulting polymer from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline compound, to thereby neutralize the carboxyl groups in the polymer.

20 reaction formula:



In the method of the present invention, the solution of the

quaternary ammonium carboxylate thus formed in the manner as mentioned above is thereafter dispersed in water, to which is added an unsaturated monomer component. In this process, the unsaturated monomer component to be subjected to polymerization in the next step may be added to the solution of the quaternary ammonium carboxylate prior to dispersing the carboxylate solution in water, or, alternatively, the solution of the quaternary ammonium carboxylate is first dispersed in water and thereafter the monomer component may be added to and dispersed in the aqueous dispersion of the quaternary ammonium carboxylate.

The amount of water to be used for the aqueous dispersion shall be determined, depending on the use and the object of the aqueous coating composition to be finally obtained herein and on the coating system to be applied to the composition. In general, however, the amount of water in question may well be such that the solid content of the coating composition can be from 10 to 80 % by weight.

The unsaturated monomer component to be added to the system of the present invention shall comprise an unsaturated compound having at least one unsaturated group in one molecule. The unsaturated compound includes, for example, acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl acrylate, n-butyl acrylate, n-hexyl methacrylate, and lauryl methacrylate; unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, itaconic acid, fumaric acid, maleic acid, citraconic acid, and cinnamic acid; and vinyl monomers such as acrylamide, styrene, vinyl acetate, and acrylonitrile. In

general, two or more of them are combined in consideration of the stability of the aqueous coating composition to be finally obtained herein and of the characteristics of the cured film to be formed from the composition.

5           In the present invention, it is indispensable that at least one unsaturated monomer to be polymerized comprises an unsaturated carboxylic acid having at least one carboxyl group and at least one unsaturated group in one molecule. The amount to be used of the unsaturated carboxylic acid having at least one  
10           carboxyl group and at least one unsaturated group in one molecule has a great influence on the dispersibility in water of the resin to be obtained, and the rheology thereof. In the method of the present invention, the relationship between the amount to be used of the unsaturated carboxylic acid having at least one carboxyl  
15           group and at least one unsaturated group in one molecule and the dispersibility in water of the resin to be obtained depends on the molecular weight of the starting epoxy resin from which the modified epoxy resin having quaternary ammonium hydroxide groups is derived. However, in order to obtain a resin having good  
20           dispersibility in water, the amount of the unsaturated carboxylic acid to be used must be such that the carboxyl content of the acid is from 1.5 to 6.0 times by mole of the quaternary ammonium hydroxide content of the epoxy resin. If the amount is less than this range, it is difficult to obtain a resin with good  
25           dispersibility in water and to obtain an aqueous coating composition with good storage stability. If, on the other hand, the amount is over the range, the characteristics, especially the water-resistance of the cured film to be formed from the



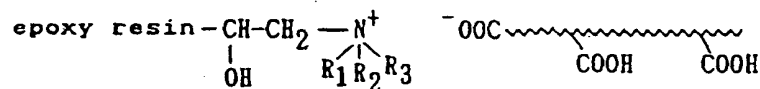
coating composition are poor.

Next, a radical polymerization initiator is added to the thus-obtained aqueous dispersion comprising the modified epoxy resin having quaternary ammonium carboxylate groups and the  
5 unsaturated monomer component comprising indispensably an unsaturated compound having at least one carboxyl group and at least one unsaturated group in one molecule, and then heated, whereby the unsaturated compound in the aqueous dispersion is polymerized.

10 The polymerization is effected generally at a temperature falling between 50°C and 100°C for from 15 minutes to 3 hours. In order to efficiently promote it, the polymerization is preferably effected in an inert gas stream, such as nitrogen or argon. The radical polymerization initiator to be employed  
15 herein includes, for example, peroxides such as benzoyl peroxide, and lauroyl peroxide, as well as azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), potassium persulfate, and ammonium persulfate, which, however, are not limitative. In addition, also employable are redox initiators, such as a  
20 combination of hydrogen peroxide and a ferrous salt, and a combination of a persulfate and acidic sodium sulfite.

In the method of the present invention, the unsaturated compound having at least one carboxyl group and at least one unsaturated group in one molecule is neutralized at the carboxyl  
25 group in the molecule, with ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline substance, during or after the polymerization. We, the present inventors have found that, when a radical polymerization initiator is added

to the aqueous dispersion of the quaternary ammonium carboxylate and the unsaturated compound having at least one unsaturated group in one molecule, and heated to polymerize the unsaturated compound in the dispersion, then an epoxy resin grafted with a carboxyl-containing acrylic polymer via a quaternary ammonium group, such as that shown in the following formula, is formed, the resin thus formed is essentially insoluble in water and therefore coagulates during the polymerization, and the resulting coagulate changes to a water-dispersible resin if neutralized with an amine or an alkali. As a result of these findings, we have completed the present invention. Specifically, after having found that, if an alkali is added to the polymerization system, after the formation of the coagulate, to thereby re-disperse the coagulate, or if an alkali is added thereto at the initial stage of the formation of the coagulate or, that is, in the course of the polymerization, it is possible to obtain a stable, water-dispersible resin, we have completed the present invention.



The alkaline substance to be employed herein for this purpose includes, for example, ammonia; primary amines such as monomethylamine, monoethylamine, n-butylamine, sec-butylamine, and n-amylamine; secondary amines such as dimethylamine, diethylamine, di-n-butylamine, dioctylamine, and diethylenetriamine; tertiary amines such as trimethylamine, triethylamine, tri-

isopropanolamine, ethyldiethanolamine, dimethylethanolamine, and triethanolamine; aniline, morpholine, toluidine, and pyridine; and also inorganic alkalis such as sodium hydroxide, potassium hydroxide, lithium hydroxide, and sodium carbonate. However, these are not limitative. The amount of the alkaline substance to be added is from 0.2 to 3.0 moles per mole of the carboxyl group in the polymer to be obtained through the above-mentioned polymerization. If the amount is less than this range, it is impossible to obtain a stable water-dispersible resin. If, however, it is over the range, the excess alkaline substance will cause the storage stability of the aqueous coating composition comprising the resin to deteriorate or will have a negative influence on the characteristics of the film to be finally obtained from the composition.

The water-dispersible resin thus obtained in the manner as mentioned hereinabove can be used even singly as an aqueous coating material to exhibit sufficient coating characteristics. However, in order to obtain a tougher film using the resin, it is desirable to add to the resin a curing agent of a phenolic resin or an amino resin.

The amino resin capable of being added to the resin of the invention includes, for example, partially butylated or methylated melamine, hexamethoxymethylmelamine, hexaethoxymethylmelamine, benzoguanamine, butylated benzoguanamine, acetoguanamine, partially or wholly butylated urea, triazine derivatives, and mixtures of these. The phenolic resin capable of being used as the curing agent in the present invention includes, for example, phenol-formaldehyde resins, resol-type

phenolic resins, novolak-type phenolic resins, bisphenol A-type resol resins, and partially butyl-etherified phenolic resins. Also employable as the curing agent is a reaction product of phenol or cresol with formaldehyde.

5           If the curing agent is used, its amount to be added is preferably from 3 to 50 % by weight relative to the solid content of the aqueous coating composition comprising the water-dispersible resin. If the amount is less than this range, the characteristics, especially the hot water-resistance of the  
10       coating film to be obtained will be often poor. If, on the other hand, it is over the range, it is difficult to obtain a stable, aqueous coating composition comprising the water-dispersible resin.

          The aqueous coating composition comprising the water-  
15       dispersible resin of the present invention can be applied to metallic substrates either directly or, if desired, after having formed an undercoat on the substrates, or after having shaped the substrates, according to any known coating method of, for example, roll coating, spray coating, dip coating, or brush  
20       coating. The thickness of the coating film to be formed from the composition is not specifically defined, provided that the metallic substrates are uniformly coated with the composition. The preferred thickness of the coating film may be generally from 1 to 50  $\mu\text{m}$ , though it varies depending on the use and the object  
25       of the metallic substrates coated.

          After having been applied to metallic substrates, the aqueous coating composition of the present invention is thermally cured at a temperature falling between 80°C and 240°C for from

1 to 30 minutes. If the curing temperature is lower than this range, the film cannot be completely cured so that it cannot attain the object of protecting the metallic substrates. If, on the other hand, it is over the range, the properties of the film to be finally obtained are worsened and the metallic substrates are deteriorated.

#### INDUSTRIAL APPLICABILITY

As has been described hereinabove, it is possible, according to the present invention, to prepare a stable water-dispersible resin while using a reduced amount of an organic solvent or not using any organic solvent, and also to provide an aqueous coating composition comprising the water-dispersible resin, which can form on metallic substrates a protective film having excellent characteristics.

The present invention is described in more detail hereinunder with reference to the following examples, which, however, are not intended to restrict the scope of the present invention.

#### EXAMPLES

##### (Example 1) Production of Water-Dispersible Resin

200 g (0.1 equivalents) of a bisphenol A-type epoxy resin, YD-017 (epoxy equivalent=1927, produced by Toto Chemicals Co.) was dissolved in 86 g of n-butoxyethanol. Next, 9.3 g (0.1 moles) of dimethylethanolamine and 10 g of water were added thereto and reacted for 3 hours at 60°C, thereby converting the epoxy groups in the epoxy resin into quaternary ammonium hydroxide groups. 30 g (0.42 moles) of acrylic acid was added to the solution of the quaternary ammonium hydroxide-containing

modified epoxy resin, and stirred for 30 minutes at 80°C thereby converting the quaternary ammonium hydroxide groups into quaternary ammonium carboxylate groups. Next, 38 g of methyl methacrylate and 20 g of ethyl acrylate were added thereto, and  
5 stirred, and then 586 g of water was added thereto. Thus was obtained a semi-transparent, aqueous dispersion of quaternary ammonium carboxylate-containing modified epoxy resin/acrylic monomer. As a polymerization initiator, 1 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added to the resulting aqueous  
10 dispersion, which was then subjected to polymerization at 80°C in a nitrogen stream. 40 minutes after the addition of the polymerization initiator, 30 ml of aqueous 28 % ammonia was added to this, with which the carboxyl groups therein were neutralized. After polymerization for 1 hour at 80°C, obtained was a stable  
15 water-dispersible resin. Even after having been stored at room temperature for 1 month or longer, the water-dispersible resin thus obtained gave neither precipitate nor coagulate of the resin component.

(Example 2) Production of Water-Dispersible Resin

20 100 g (0.05 equivalents) of a bisphenol A-type epoxy resin, YD-017 (epoxy equivalent=1927, produced by Toto Chemicals Co.) was dissolved in 60 g of n-butoxyethanol. Next, 5.0 g (0.056 moles) of dimethylethanolamine and 10 g of water were added thereto, stirred at room temperature, and then left static at  
25 room temperature for 10 hours. Thus was obtained a solution of a quaternary ammonium hydroxide-containing modified epoxy resin. 5.1 g (0.056 moles) of lactic acid was added to the solution, and stirred for 30 minutes at 70°C, thereby converting the quaternary

ammonium hydroxide groups in the modified resin into quaternary ammonium carboxylate groups. Next, 270 g of water was added to this, which gave an almost transparent dispersion. 20 g of methyl methacrylate, 10 g of ethyl acrylate and 12 g of acrylic acid were added to this dispersion, and 1.3 g of a polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto and subjected to polymerization at 80°C in a nitrogen stream. After one hour, a coagulate was formed in the system. 12 g of dimethylethanolamine was added thereto, by which the coagulant was wholly re-dispersed to give a creamy, water-dispersible resin having low viscosity. As in Example 1, the resin dispersion obtained herein was stable.

(Example 3) Production of Water-Dispersible Resin

100 g (0.056 equivalents) of a bisphenol a-type epoxy resin, Epicoat 1007 (epoxy equivalent=1789, produced by Yuka Shell Co.) was dissolved in 67 g of carbitol, and 5 g (0.056 moles) of dimethylethanolamine and 10 g of water were added thereto, and stirred for 3 hours at 50°C to obtain a solution of a quaternary ammonium hydroxide-containing modified epoxy resin. To this solution was added 15.8 g (0.18 moles) of methacrylic acid and stirred for 1 hour at 60°C, whereby the quaternary ammonium hydroxide groups in the modified resin were converted into quaternary ammonium carboxylate group. Next, 180 g of water was added thereto, and 0.5 g of a polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto, and subjected to polymerization at 80°C in a nitrogen stream. 30 minutes after the start of the polymerization, 8 g of aqueous 28 % ammonia was added to the reaction system, and the

polymerization was continued further. After one hour, obtained was a white aqueous dispersion of a water-dispersible resin.

(Example 4) Production of Water-Dispersible Resin

200 g (0.08 equivalents) of a bisphenol A-type epoxy resin, YD-019 (epoxy equivalent=2467, produced by Toto Chemicals Co.) was dissolved in 120 g of n-butoxyethanol. Next, 7.1 g (0.08 moles) of dimethylethanolamine and 15 g of water were added thereto, and reacted for 3 hours at 60°C to obtain a solution of a quaternary ammonium hydroxide-containing modified epoxy resin. 5.0 g of acetic acid was added to this solution, and stirred for 30 minutes at 80°C to thereby convert the quaternary ammonium hydroxide groups in the modified resin into quaternary ammonium carboxylate groups. Next, 433 g of water was added thereto, and an almost transparent dispersion was obtained. 38 g of methyl methacrylate, 20 g of ethyl acrylate and 22 g of acrylic acid were added to this dispersion, and 1.3 g of a polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto and subjected to polymerization at 80°C in a nitrogen stream. After one hour, a coagulate was formed in the system. 15 g of aqueous 28 % ammonia was added thereto, by which the coagulant was wholly re-dispersed to give a creamy, water-dispersible resin having low viscosity. As in Example 1, the resin dispersion obtained herein was stable.

(Example 5) Production of Water-Dispersible Resin

200 g (0.1 equivalents) of a bisphenol A-type epoxy resin, YD-017 (epoxy equivalent=1927, produced by Toto Chemicals Co.) was dissolved in 134 g of n-butoxyethanol. Next, 9.7 g (0.11 moles) of dimethylethanolamine and 10 g of water were added



thereto and reacted for 3 hours at 60°C, thereby converting the epoxy groups in the epoxy resin into quaternary ammonium hydroxide groups. 30 g (0.42 moles) of acrylic acid was added to the solution of the quaternary ammonium hydroxide-containing modified epoxy resin, and stirred for 30 minutes at 80°C thereby converting the quaternary ammonium hydroxide groups into quaternary ammonium carboxylate groups. Next, 58 g of methyl methacrylate was added thereto, and stirred, and then 484 g of water was added thereto. Thus was obtained a semi-transparent, aqueous dispersion of quaternary ammonium carboxylate group-containing modified epoxy resin/acrylic monomer. As a polymerization initiator, 1 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added to the resulting aqueous dispersion, which was then subjected to polymerization at 80°C in a nitrogen stream. 20 minutes after the addition of the polymerization initiator, a solution as prepared by dissolving 20 ml of aqueous 28 % ammonia in 40 ml of water was added to this, with which the carboxyl groups therein were neutralized. After polymerization for 1 hour at 80°C, obtained was a stable water-dispersible resin. Even after having been stored at room temperature for 1 month or longer, the aqueous dispersion of the resin thus obtained gave neither any precipitate nor any coagulate.

(Example 6) Production of Water-Dispersible Resin

80 g (0.032 equivalents) of a bisphenol A-type epoxy resin, YD-019 (epoxy equivalent=2477, produced by Toto Chemicals Co.) was dissolved in 57 g of n-butoxyethanol. To this were added 2.3 g of acrylic acid, 2.9 g of dimethylethanolamine, 0.6 g of water, and 0.002 g of p-methoxyhydroquinone, and reacted for 2 hours at

90°C. Next, 292 g of water was added thereto to obtain a semi-transparent dispersion. 16 g of methyl methacrylate and 8.5 g of methacrylic acid were added to this dispersion, and 1 g of a polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto, and subjected to polymerization at 80°C in a nitrogen stream.

After one hour, the reaction product coagulated. When 8.0 g of dimethylethanolamine was added thereto, the coagulate was wholly re-dispersed to give a stable water-dispersible resin.

10 (Comparative Example 1)

200 g (0.1 equivalents) of a bisphenol A-type epoxy resin, YD-017 (epoxy equivalent=1927, produced by Toto Chemicals Co.) was dissolved in 86 g of n-butoxyethanol. Next, 9.3 g (0.1 moles) of dimethylethanolamine and 10 g of water were added thereto, and reacted for 3 hours at 60°C, thereby converting the epoxy groups in the resin into quaternary ammonium hydroxide groups. 38 g of methyl methacrylate and 20 g of ethyl acrylate were added to the solution of the quaternary ammonium hydroxide-containing modified epoxy resin thus obtained, and stirred, and then 586 g of water was added thereto. However, the quaternary ammonium hydroxide-containing modified epoxy resin was not dispersed in water. From this, it is understood that the conversion of the quaternary ammonium hydroxide groups in the resin into quaternary ammonium carboxylate groups with an acid is indispensable in order to obtain a resin with good dispersibility in water.

(Comparative Example 2) Production of Water-Dispersible Resin

200 g (0.1 equivalents) of a bisphenol A-type epoxy resin,

YD-017 (epoxy equivalent=1927, produced by Toto Chemicals Co.) was dissolved in 134 g of n-butoxyethanol. Next, 9.7 g (0.11 moles) of dimethylethanolamine and 10 g of water were added thereto, and reacted for 3 hours at 60°C, thereby converting the epoxy groups in the resin into quaternary ammonium hydroxide groups. 30 g (0.42 moles) of acrylic acid was added to the solution of the quaternary ammonium hydroxide-containing modified epoxy resin thus obtained, and stirred for 30 minutes at 80°C, thereby converting the quaternary ammonium hydroxide groups in the modified resin into quaternary ammonium carboxylate groups. Next, 58 g of methyl methacrylate was added thereto, and stirred, and then 484 g of water was added thereto to obtain a semi-transparent aqueous dispersion of quaternary ammonium carboxylate group-containing modified epoxy resin/acrylic monomer. A solution as prepared by dissolving 20 ml of aqueous 28 % ammonia in 40 ml of water was added to the resulting aqueous dispersion to thereby neutralize the carboxyl groups therein, whereupon the dispersion immediately coagulated just after the addition of the aqueous ammonia thereto and the reaction could not be continued further more.

(Comparative Example 3)

200 g (0.1 equivalents) of a bisphenol A-type epoxy resin, YD-017 (epoxy equivalent=1927, produced by Toto Chemicals Co.) was dissolved in 86 g of n-butoxyethanol. Next, 9.3 g (0.1 moles) of dimethylethanolamine and 10 g of water were added thereto, and reacted for 3 hours at 60°C, thereby converting the epoxy groups in the resin into quaternary ammonium hydroxide groups. 30 g of acrylic acid was added to the solution of the

quaternary ammonium hydroxide-containing modified epoxy resin thus obtained, and stirred for 30 minutes at 80°C, thereby converting the quaternary ammonium hydroxide groups in the modified resin into quaternary ammonium carboxylate groups.

5 Next, 38 g of methyl methacrylate and 20 g of ethyl acrylate were added thereto, and stirred, and then 1 g of a polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) was added to this, which was thus subjected to polymerization at 80°C in a nitrogen stream.

10 Ten minutes after the start of the polymerization, the reaction product gelled.

(Comparative Example 4)

80 g (0.03 equivalents) of a bisphenol A-type epoxy resin, YD-019 (epoxy equivalent=2497, produced by Toto Chemicals Co.)  
15 was dissolved in 53 g of n-butoxyethanol. Next, 2.8 g (0.031 moles) of dimethylethanolamine and 0.6 g of water were added thereto, and reacted for 1 hour at 80°C to obtain a solution of a quaternary ammonium hydroxide-containing modified epoxy resin. To this solution was added 2.0 g (0.033 moles) of acetic acid,  
20 and stirred for 30 minutes at 80°C thereby converting the quaternary ammonium hydroxide groups in the modified resin into quaternary ammonium carboxylate groups. Next, 374 g of water was added thereto to obtain a semi-transparent dispersion. To this were added 10.2 g of methyl methacrylate and 6.8 g of n-butyl  
25 acrylate, and 1 g of a polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) was added to this, which was thus subjected to polymerization at 80°C in a nitrogen stream. After having been reacted for 30 minutes at 80°C, this gave a semi-

transparent dispersion. Since the viscosity of the dispersion thus obtained was too low, it was difficult to use it as a coating material.

(Example 7) Preparation of Aqueous Coating Compositions and  
5 Evaluation of Their Properties

The water-dispersible resins as obtained in Examples 1 and 5 were directly used as coating materials, or each were combined with the curing agent as shown in Table 1 and formulated into aqueous coating compositions. The amount of the curing agent  
10 added was 10 % by weight relative to the solid resin content of each water-dispersible resin. In addition, the water-dispersible resin as obtained in Comparative Example 4 was directly used as a coating material, or was formulated into an aqueous coating composition in the same manner as above. These resin  
15 compositions each were applied onto a tin plate, using a wire bar, at a dry film thickness of 10  $\mu\text{m}$ , and then cured at 200°C for 12 minutes.

To determine the degree of curing thereof, each sample was subjected to a rubbing test up to 100 cycles, in which the sample  
20 was rubbed two times with a cotton soaked with methyl ethyl ketone (MEK) in one cycle. The number of cycles after which the film was damaged was counted. To determine the adhesiveness of each film to the plate, each sample was subjected to a so-called cross-cut tape-peeling test, in which cross-cuts of 1 mm were  
25 formed on the film with a cutter knife, and an adhesive cellophane tape was attached thereto and then peeled off. The adhesiveness was evaluated according to 6-rank evaluation, in which "0" indicates that the film was not peeled along with the

adhesive tape, and "5" indicates that the film was completely peeled. In addition, each coated sample was subjected to a boiling test, in which it was left in an autoclave at 131°C for 30 minutes whereupon the condition of the outward appearance of the coating film was observed. The test results are shown in Table 1.

Table 1

Water-Dispersible Resin	Curing Agent	MEK Resistance	Cross-Cut Tape-Peeling Test	Boiling Resistance
Example 1	No	>100	0	No Change
Example 1	SFC 099	>100	0	No Change
Example 1	Cymel 303	>100	0	No Change
Example 5	No	>100	0	No Change
Example 5	PR-217	>100	0	No Change
Comparative Example 4	No	1	-	-
Comparative Example 4	Cymel 303	2	-	-

SFC 099: Phenolic Resin, produced by Schenectady Co.

Cymel 303: Hexamethoxymethylolmelamine, produced by Mitsui Cyanamid Co.

PR-217: Phenolic Resin, produced by Hoechst AG.

## CLAIMS

1. A method for preparing a water-dispersible resin comprising the steps of:

(a) reacting an epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000 with from 1 to 1.5 equivalents, per equivalent of the epoxy resin, of a tertiary amine, in the presence of water in a solvent, to prepare a modified epoxy resin having at least two quaternary ammonium hydroxide groups in one molecule;

(b) reacting the modified epoxy resin having at least two quaternary ammonium hydroxide groups in one molecule as obtained in the previous step (a) with an organic acid having at least one carboxyl group in one molecule to prepare a modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule;

(c) dispersing in water the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule as obtained in the previous (b);

(d) polymerizing, in the aqueous dispersion of the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule as obtained in the previous step (c), at least one unsaturated monomer component that indispensably comprises an unsaturated compound having at least one unsaturated group and at least one carboxyl group in one molecule; and

(e) adding to the resulting polymer from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a



primary amine, a secondary amine, a tertiary amine or an inorganic alkaline compound, to thereby neutralize the carboxyl groups in the polymer.

2. A method for preparing a water-dispersible resin comprising the steps of:

(i) reacting an epoxy resin having at least two 1,2-epoxy groups in one molecule and having an epoxy equivalent of from 100 to 5,000 with from 1 to 1.5 equivalents, per equivalent of the epoxy resin, of a tertiary amine and an organic acid, in the presence of water in a solvent, to prepare a modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule;

(ii) dispersing in water the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule as obtained in the previous step (i);

(iii) polymerizing, in the aqueous dispersion of the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule as obtained in the previous step (ii), at least one unsaturated monomer component that indispensably comprises an unsaturated compound having at least one unsaturated group and at least one carboxyl group in one molecule; and

(iv) adding to the resulting polymer from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline compound, to thereby neutralize the carboxyl groups in the polymer.

3. The method for preparing a water-dispersible resin

as claimed in claim 1, wherein the organic acid to be used in the step (b) is an unsaturated carboxylic acid having both at least one unsaturated group and at least one carboxyl group in one molecule.

5           4. The method for preparing a water-dispersible resin as claimed in claim 2, wherein the organic acid to be used in the step (1) is an unsaturated carboxylic acid having both at least one unsaturated group and at least one carboxyl group in one molecule.

10           5. The method for preparing a water-dispersible resin as claimed in claim 1 or 2, wherein at least one unsaturated monomer component that indispensably comprises an unsaturated compound having at least one unsaturated group and at least one carboxyl group in one molecule is added to the modified  
15 epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule, then water is added to the resulting mixture to prepare an aqueous dispersion of the mixture, and the aqueous dispersion is subjected to polymerization.

20           6. The method for preparing a water-dispersible resin as claimed in claim 1 or 2, wherein the modified epoxy resin having at least two quaternary ammonium carboxylate groups in one molecule is dispersed in water, then at least one  
25 unsaturated monomer component that indispensably comprises an unsaturated compound having at least one unsaturated group and at least one carboxyl group in one molecule is added to the resulting dispersion, and the dispersion thus obtained is subjected to polymerization.

7. The method for preparing a water-dispersible resin as claimed in claim 1 or 2, wherein from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline compound is added to the reaction system in the course of polymerization, to thereby neutralize the carboxyl groups of the polymer.

8. The method for preparing a water-dispersible resin as claimed in claim 1 or 2, wherein from 0.2 to 3.0 moles, per carboxyl equivalent of the polymer, of ammonia, a primary amine, a secondary amine, a tertiary amine or an inorganic alkaline compound is added to the reaction system after polymerization, to thereby neutralize the carboxyl groups of the polymer.

9. An aqueous coating composition comprising a water-dispersible resin as produced in the method of claim 1 or 2, along with a phenolic resin or an amino resin.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/JP 96/02987

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08L63/00 C08F283/00 C08L51/08 C09D151/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08L C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 83 03613 A (DU PONT) 27 October 1983 see page 9, line 29 - page 12, line 23 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 195 (C-1049), 16 April 1993 & JP 04 345610 A (DAINIPPON INK & CHEM INC), 1 December 1992, see abstract	
A	& DATABASE WPI Section Ch, Week 9302 1 December 1992 Derwent Publications Ltd., London, GB; Class A21, AN 93-015364 see abstract --- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-8303613	27-10-83	US-A- 4423165	27-12-83
		AU-B- 557446	18-12-86
		AU-A- 1339783	04-11-83
		CA-A- 1195036	08-10-85
		EP-A- 0105293	18-04-84
		GB-A- 2127415	11-04-84
		HK-A- 56986	08-08-86
		JP-B- 4005072	30-01-92
		JP-T- 59500565	05-04-84